PART I
PART II will appear in the June issue.

UNCOVERING THE REALITIES OF SIMULATION

RAJEEV AGARWAL, YAU-KUN LI, OSCAR SANTOLLANI, AND MARCO A. SATYRO,
VIRTUAL MATERIALS GROUP, INC.
ANDREW VIELER,
SIMULATION ENGINEERING

Running sophisticated process simulations does not guarantee correct results. You need to understand the thermodynamic assumptions underlying the program and how to ensure proper application.

TODAY, CHEAP COMPUTER POWER allows virtually any engineer to have enough capability to simulate large flowsheets with considerable detail on the desktop. Process flowsheet simulators having sophisticated user interfaces, large physical properties databanks, and many thermodynamic models are now commonplace.

Several simulators also feature programmability using languages and external programs, thus allowing virtually unlimited flexibility in manipulating the available physical properties, together with the ability of defining new unit operations without depending upon the simulation vendors for any significant proprietary information. For example, a comprehensive thermodynamic package for the simulation of sulfuric acid plants is available *(1)* to run with generic process simulators as a third-party add-on.

Readily available, extremely powerful programming languages, such as Visual Basic, provide comprehensive data access using relational databases, powerful object manipulation using the operating system, and extremely rich sets of add-ons, from graphing packages to control tuning software. These tools are well integrated with larger applications, such as Microsoft's Office suite, and can be combined with process simulators to create novel applications, such as online data acquisition systems combined with real-time optimization *(2)*.

From a practical standpoint, process simulators provide a reliable platform for solving material and energy balances using variations of the sequential modular- or equation-based approaches. Albeit a few pathological problems still exist related to multiple solutions for a flowsheet and poor recycle convergence, by and large, an engineer can create a complex flowsheet with minimal difficulty using icons. The user can then drag and drop unit operations, and he or she expects it to converge without problems. In many cases, this is exactly what will happen.

Given the wide variety of available thermodynamic models and unit operations libraries available, and thousands of built-in pure-component and interaction parameters (also, the ability of automatically estimating missing physical properties and interaction parameters), it seems that most chemical processing problems can be dealt with accurately and reliably. Unfortunately, this is more of a dream than reality.

Science fiction or science fact?

In the same way that a writer can manipulate words and concepts to create stories, engineers can use simulators to generate fictional plant stories that describe how diverse substances interact in the presence of temperature, pressure, heat, and other thermodynamic quantities in the tale of synthesis and purification. Further, one may claim that the difference between a talented writer and a word pusher is the ability to create plausible stories that seemingly unfold in front of us in the real world, and we just go along for the ride.

Thus, the difference between a talented user of process simulators and a generator of case studies is the ability to generate plausible simulations bound by the reality defined by the fundamental laws of chemistry and physics. Here is where a talented author has a significantly easier task than an engineer, since an engineer has to craft a story to conform to thermodynamic laws and fluid behavior.

These laws and behavior are well known and, therefore, should be properly packaged and reliably available in simulators; thus, engineers are limited by their creativity in piecing together a flowsheet to tell a good story. Indeed, the first and second laws of thermodynamics are well understood and properly implemented in the model equations used to describe unit operations and unit operation connectivity. Thermodynamic equilibrium equations have been well known for more than a century, therefore, all is well, eh? Perhaps, not.

A trivial example

Let us say we want to model an ethanol production facility, and we specify a volume fraction of ethanol for the distillate at 0.96. This is below the azeotropic value of about 0.97 at 60°F. The simulator calculates a mass fraction of 0.950, while the correct value is 0.937. If our tower is operating at atmospheric pressure, the azeotropic composition is 0.956 mass. So, the simulator predicts a mass fraction of ethanol much closer to the azeotrope than reality, and, therefore, a harder separation than one would actually have. A tower designed using this specification will have a reflux ratio larger than necessary with corresponding larger capital and energy costs. Naturally, for another mixture close to the azeotropic point, the simulator can calculate a mass fraction further away from this point, and, depending upon the accuracy of the vapor/liquid equilibrium (VLE) model, we could have designed a tower that would never actually operate, because our distillate specification would be beyond the actual azeotrope.

Simulators generally assume that molar volumes are additive. Therefore, what the simulator does behind the scenes in a volume fraction specification is calculating the molar densities of the components at a given temperature (usually, 60°F). With that and the volume fractions, mole fractions can be calculated and, from there, mass fractions in a rather straightforward manner. The problem is that we are assuming that the molar volume of a pure component corresponds to the volume the component would have in a mixture:

Nomenclature

a	=	van der Waals equation attractive factor
a	=	Margules interaction parameter
b	=	van der Waals equation covolume
B	=	bottoms
Cp	=	isobaric heat capacity
D	=	distillate
f	=	fugacity
G	=	Gibbs free energy
H	=	Henry's law constant
H	=	enthalpy
k	=	equation of state interaction parameter
n	=	number of moles
nc	=	number of components in mixture
N	=	number of trays
P	=	pressure
P_{sat}	=	vapor pressure
R	=	gas constant
S	=	entropy
T	=	absolute temperature
V	=	Molar volume
x	=	liquid mole or volume fraction
y	=	vapor mole fraction
Z	=	compressibility factor
LK	=	light key
HK	=	heavy key

Subscripts

i, j, k	=	component index in a mixture
m	=	minimum number of trays
pure	=	pure component
solvent	=	value referring to solvent
solvSat	=	at conditions where the solvent is at its P_{sat}
v	=	volume

Superscripts

-	=	partial molar
0	=	standard state
∞	=	infinite dilution
E	=	excess
l	=	liquid
s	=	at saturation
v	=	vapor

Greek letters

α	=	relative volatility
γ	=	activity coefficient
σ	=	numerical constant

$$x_i = \frac{\frac{1}{V_i} x_{v,i}}{\sum_i \frac{1}{V_i} x_{v,i}} \quad (1)$$

Nevertheless, many times, we have a nonnegligible excess volume, and the mixture molar volume actually varies like this:

$$V = \sum_i V_i x_i + V^E(T,\vec{x}) \quad (2)$$

Equation 2 can be written using partial molar volumes:

$$V = \sum_i \bar{V}_i x_i \quad (3)$$

where the partial molar volume can be thought of as an effective molar volume a component has in a given mixture. So, we would be tempted to write our molar fraction equation as:

$$x_i = \frac{\frac{1}{\bar{V}_i} x_{v,i}}{\sum_i \frac{1}{\bar{V}_i} x_{v,i}} \quad (4)$$

Naturally, this has a catch. The partial molar volume is a function of the mole fraction (as well as temperature and, to a lesser extent, pressure). Therefore, we have an iterative solution in mole fraction when specifying volume fractions for systems that present excess volumes. Usually, simulators do not take this into consideration (for good reasons, as this is usually small for many important systems), but, sometimes, this may cost you dearly depending on how you got your specifications and how you entered them in the simulator.

The "heavy in the top" caper

Moura and Carneiro *(3)* describe a problem where a commercial simulator was used for the evaluation of a 1,3-butadiene purification tower. It is well known that 1,2-butadiene is less volatile than 1,3-butadiene, and, as expected, 1,2-butadiene would leave mostly through the tower bottoms. Still, the simulation predicted that 1,2-butadiene would leave through the top. This is a simple system for which experimental data and reasonable thermodynamic models are available. Why the error?

The simulator used critical properties predicted by the Cavett correlation. When applying these estimates, the thermodynamic model would predict that 1,2-butadiene was volatile enough to leave in the distillate. If we tabulate the physical properties of 1,2-butadiene used by the simulator against the physical properties recommended by AIChE's Design Institute for Physical Property Data (DIPPR), it is evident that the acentric factor was incorrect (Table 1). We will see that acentric factors are a fundamental property when using equation(s) of state (EOS), because they correlate the vapor pressures calculated by pure components.

A tale of multiple solutions

This example, also from Moura and Carneiro, demonstrates how the results depend not only on the thermodynamic model being used, but also on how it is implemented. Figure 1 shows a hydrotreating unit, in which the feeds are liquid oil and hydrogen. These are mixed with a hydrogen recycle to guarantee a minimum mass ratio of hydrogen-to-oil for the reactors. The mixed feed and recycle are heated to the desired temperature for Reactor 1. The temperature increases after Reactor 1 and, to cool the effluent to the desired inlet temperature for Reactor 2, a cold gas stream is used. The effluent from Reactor 2 is cooled, and the hydrogenated oil leaves the system and the excess hydrogen is compressed and returned to the system as recycle gas.

Two simulation controllers were used in the model. One controls the inlet temperature for the feed to Reactor 2, determining the cooling-gas flow rate and the other sets the hydrogen/oil ratio at the inlet of Reactor 1, establishing the treating-gas flow rate. Two cases were considered, one in which the oil is very reactive, and another in which the feed has a low reactivity. The compressor was sized for the first case, and the simulations were set up to maintain a constant flow rate thorough the compressor. Since the recycle-gas flow rate is equal to the treating-gas flow rate plus the cooling-gas flow rate, the hydrogen/oil ratio controller was replaced by a recycle gas flow controller for the second simulation.

Nevertheless, Case 1 was repeated using Case 2's controller configuration. In both instances, the reactant conversion was fixed to an identical value. This time, the simulator found a different solution for Case 1, with a hydrogen/oil ratio below the minimum required.

The cause was an incorrect root calculation for the compressibility factor for some combinations of pressure, temperature, and composition for the Lee-Kesler *(6)* correlation, used to determine enthalpies. This was a problem with the particular implementation of the root calculation by the simulator, not the basic thermodynamic model. This incorrect root assignment in turn caused the simulator to converge on an incorrect flow rate, as shown in Figure 2, where the inlet and outlet stream enthalpies are plotted vs. the molar flow rate of treating gas. Note the discontinuity in the outlet enthalpy shown as a "bump" in the curve.

Table 1. Physical properties of 1,2-butadiene.

Physical Property	Cavett *(4)*	DIPPR *(5)*
Critical Temperature, °R	824.5	799.2
Critical Pressure, psia	589.7	652.7
Acentric Factor	0.0987	0.2509

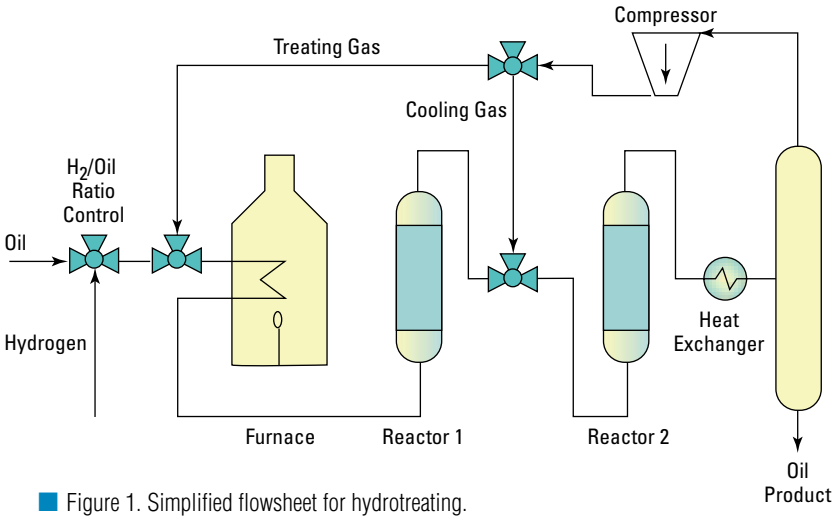

Figure 1. Simplified flowsheet for hydrotreating.

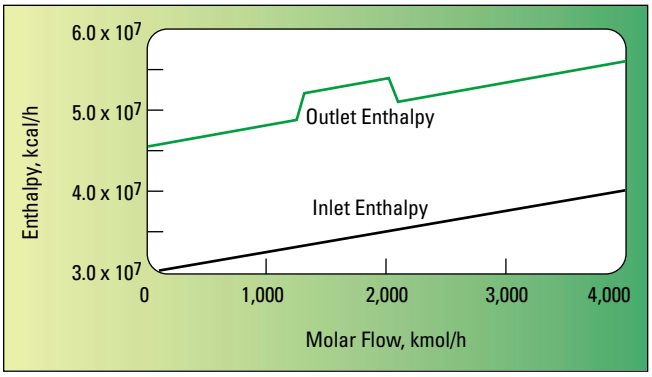

Figure 2. Incorrect root calculation yields bump in the outlet enthalpy curve.

An energy generator at your fingertips

Simulators capable of handling multiple unit operations or flowsheets, each sporting its own thermodynamic options, allow the simulation of some complex situations. Nevertheless, these compounded simulations may find their way into other realms, which their initial creators did not consider. For example, the simulation may be the basis for a plant-wide optimization.

So far so good. But, usually one can use any variables for optimization, and, perhaps, the simulation is being used for a heat integration study. For one reason or another, one wants to minimize (or maximize) the enthalpy content of a stream. If this stream comes from a unit operation that has a different enthalpy basis from the main flowsheet (for example, it uses a different thermodynamic model), then you will have two streams. One is the outlet of the unit operation in the unit operation space and the other the outlet of the unit operation in the flowsheet space.

These will have different enthalpies! Therefore, depending on how your optimization is set up, the optimizer may start moving variables in a strange way, because it will be trying to take advantage of a purely artificial condition introduced by two inconsistent models.

This can also be a problem when different vaporizations or number of liquid phases are calculated for the "same" stream in two sections of the flowsheet that use different thermodynamic models. For example, if a recycle is based on a stream existing after leaving a flash and the stream is empty (*i.e.*, in the flowsheet section you are interested in), it may cause lots of grief until you can actually debug the flowsheet and find the reason why, for some conditions, the simulation converges like a charm and, afterwards, it goes haywire.

Changing results depending on release date

Process simulation companies face an excruciating problem. If better correlations or data appear, the initial tendency is to go and refine the current models. Nevertheless, if the models are refined and new default values used, then the simulation results will change. That is a problem when guaranteeing equipment or design calculations. Although we do not have a general answer, Yang *et al. (7)* show significant differences between the results for the simulation of a simple *i*-C_5/*n*-C_5 splitter for three commercial simulators, including three instances (one in each simulator) where the new version of the simulator would not converge on solutions it had previously achieved.

Reality is your interpretation of it

Why is it that we have very fast computers, rich flowsheeting environments, large unit operations libraries, advanced convergence techniques, comprehensive pure-component and interaction-parameter databases, and still we have unreliable simulations? The reason lies in the scope of problems solved by users of simulations and the degree of knowledge and rigor that can be provided by chemical engineering science.

Chemical engineering solves complex problems that result from the sheer size of the number of interacting molecules, even in the simplest systems. This fosters the need to simplify the models so as to use statistical mechanics. Statistical methods can provide exact answers only for the simplest cases, and, to extend their use for more realistic calculations, we usually have to provide some empirical information to subsidize the theoretical model. This can be a humble set of critical properties used since the 19th century by van der Waals or some type of complex intermolecular interaction energy.

Most of the available models for chemical engineers are based on some empirical information, thus relying on data that are applicable only to certain conditions. Because most models are not truly theoretically based, thereby ensuring consistency across many boundary conditions (such as fundamental theoretical models used in physics), one cannot in general say *a priori* how a ther-

modynamic model will behave when extrapolated beyond the region in which data were available for determining its empirical parameters.

Therefore, notwithstanding the computer power, richness of unit operation libraries and databases, and numerical sophistication, users of simulation are, in general, treading a thin line separating fact from fiction. This line has nothing to do with the rigorousness of the formulation of the material and energy balance equations, which are handled correctly by most simulators, but rather the line defining fact and fiction as predicted by the thermodynamic package used for simulation. Determining where your simulation becomes science fiction tells if your work is a reasonable guess of how nature is going to behave or if your work is simply bad fiction. The remainder of this article discusses some practical guidelines for maximizing your chance of writing better simulation stories.

Of mice and mixtures

Simulation of chemical processes normally involves finding the properties of pure components and some thermodynamic descriptor for the mixture (*e.g.*, EOS and mixing rules, activity coefficient expressions, and the like). We start by taking a look at the basics of phase equilibria as the background to which we will pin down the importance of related physical properties, pure-component and otherwise.

Look at the basic expression for phase equilibrium written as the equality of fugacities across phases:

$$\phi_i^v y_i P = \phi_i^l x_i P \tag{5}$$

We can write the activity coefficient as:

$$\gamma_i^l = \frac{\phi_i^l}{\phi_{i,\,pure}^l} \tag{6}$$

and substituting into Eq. 5 we get:

$$\phi_i^v y_i P = \gamma_i \phi_{i,\,pure}^l x_i P \tag{7}$$

Note that the vast majority of activity coefficient models do not take into account their dependency on pressure, while Eq. 6 is general and can be conveniently applied to EOS. Thus, we recast the activity coefficient using an exact thermodynamic relationship:

$$\gamma_i^P = \gamma_i^{Pref} \exp\left(\int_{P_{ref}}^{P} \frac{\bar{v}_i}{RT} dP\right) \tag{8}$$

where P_{ref} is some reference pressure, usually around 1 atm, at which pressure effects can be neglected.

Using the definition of fugacity coefficient we have:

$$\phi_{i,\,pure} = \frac{f_{i,\,pure}}{P} \tag{9}$$

Casting Eq. 7 into the shape shown in textbooks:

$$\phi_i^v y_i P = \gamma_i x_i f_{i,\,pure}^l \exp\left(\int_{P_{ref}}^{P} \frac{\bar{v}_i}{RT} dP\right) \tag{10}$$

We dropped the superscript P_{ref} for simplicity from the activity coefficient; its dependency on pressure is given by the exponential term.

Using the definition of fugacity, integration up to the saturated pure component state brings us to:

$$\phi_i^v y_i P = \gamma_i x_i P_i^v \phi_i^s \times \exp\left(\int_{P_{sat,i}}^{P_{ref}} \frac{v_i}{RT} dP\right) \times \exp\left(\int_{P_{ref}}^{P} \frac{\bar{v}_i^l}{RT}\right) \tag{11}$$

When the pressure is low and conditions are far from the critical state, the activity coefficient is essentially independent of pressure, and it is common to set the reference pressure to be the saturation pressure of component *i*, $P_{sat,i}$, and Eq. 11 is cast in the form that is usually shown in textbooks:

$$\phi_i^v y_i P = \gamma_i x_i P_i^v \phi_i^s \exp\left(\int_{P_{ref}}^{P} \frac{\bar{v}_i}{RT} dP\right) \tag{12}$$

For convenience in here we will set the reference pressure to 0. Eq. 11 is written as:

$$\phi_i^v y_i P = \gamma_i x_i P_i^v \phi_i^s \exp\left(-\int_{0}^{P_{sat,i}} \frac{v_i}{RT} dP\right) \times \exp\left(\int_{P_{ref}}^{P} \frac{\bar{v}_i}{RT} dP\right) \tag{13}$$

Equation 13 is mathematically equivalent to Eq. 5, and, as long as its terms are correctly computed, it can be used up to the critical point of the mixture (a fact sometimes brushed aside to justify the use of EOS in place of activity-coefficient-based models). Therefore, what do we gain in going from Eq. 5 to Eq. 13? From a physical point of view, we gain insight into the different properties necessary to compute the phase equilibrium. From a modeling point of view, we get two models, one for the liquid and another for the vapor, which can be used separately (this is the counterpoint to the statement above about activity-coefficient models — usually one does the modeling without worrying about consistency around the critical point).

Let us write Eq. 11 in the way normally used for flash calculations:

$$y_i = \left(\frac{P_{sat,\,i}}{P}\right)\frac{\phi_i^{s}}{\phi_i^{v}}\exp\left(-\int_0^{P_{sat,i}}\frac{v_i}{RT}\,dP\right)\times \exp\left(\int_{P_{ref}}^{P}\frac{\bar{v}_i}{RT}\,dP\right)\gamma_i x_i \qquad (14)$$

At modest pressures (with the exception of associating mixtures in the vapor phase, such as carboxylic acid mixtures), the ratio $\left(\phi_i^{s}/\phi_i^{v}\right)$ is close to 1, as well as the terms $\exp\left(\int_0^{P_{sat,i}} -\frac{v_i}{RT}dP\right)$ and $\exp\left(\int_{P_{ref}}^{P}\frac{\bar{v}_i}{RT}\,dP\right)$ (normally referred to as the Poynting factor). This is illustrated in Figures 3 and 4.

The fugacity coefficient ratio is about 0.92 over the pressure range, instead of 1.0, a difference of 8% — not that negligible. Why can we manage relatively well by neglecting this term? In the exercise above, we stretched things a bit to show that these ratios are not as benign as one would initially suspect.

Recall that the maximum difference in pressure for a binary, nonazeotropic system at saturation at a fixed temperature is going to be given by the vapor pressure of the pure components, and that, for many important systems, the differences in vapor pressures for a given temperature will be much smaller. For example, for ethanol and water at 100°C, the difference in vapor pressures is about 113 kPa and the corresponding $\left(\phi_i^{s}/\phi_i^{v}\right)$ is about 0.98, better than 0.92.

How did we get the Poynting factor plot? What about the mysterious (and conveniently not mentioned) factor $\bar{v}_i$ This is the partial molar volume of Component *i*, which is a function of the system pressure, temperature, and composition. Partial molar properties are useful mathematical constructs for calculating physical properties in a way that is formally identical to molar fraction averages, as was shown in Eq. 4.

$$v = \sum_{i=1}^{nc}\bar{v}_i x_i \qquad (15)$$

The partial molar volume is not the same as the ordinary pure-component molar volume, because it has to be just right to give the right combined molar volume for the mixture. For real mixtures, there is some kind of volumetric expansion or contraction.

How was Figure 4 calculated? We assumed that the partial molar volume of Component *i* is a constant and equal to the molar volume of Component *i* at the mixture temperature. That is a harsh approximation, not even physically correct (the partial molar volume is a mixture property and we are saying that the liquid mixture is always ideal).

Why can we bypass this problem (which is done thousands of times everyday by users of process simulators)? The answer lies in the precision.

The integral in $\exp\left[\int_{P_{sat,i}}^{P}\left(\bar{v}_i/RT\right)dP\right]$ is so close to 0 for modest pressures and components well below their critical point that, despite a poor approximation, it does not matter (except when closer to the mixture's critical point).

So, how can we model systems with $\left(\phi_i^{s}/\phi_i^{v}\right)$ different than unity by not using it? After all, activity coefficient models are employed many times with the ideal gas assumption, *i.e.*, the above ratio = 1, and Poynting factors are also equal to 1. The answer is simple. The activity coefficients in Eq. 13 can absorb these effects (to a certain extent) in disguise inside the activity-coefficient interaction parameters. This is why you should be careful before using interaction parameters someone else regressed. If your conditions are quite different from those used to regress the parameters (not only pressure, but also temperature and composition), then they likely will extrapolate poorly and you will have a dangerous model in your hands.

So, now that we understand how we calculated the Poynting factor and the $\left(\phi_i^{s}/\phi_i^{v}\right)$ factor, we can proceed with the simplifications of our equilibrium equation and get into the form everyone knows:

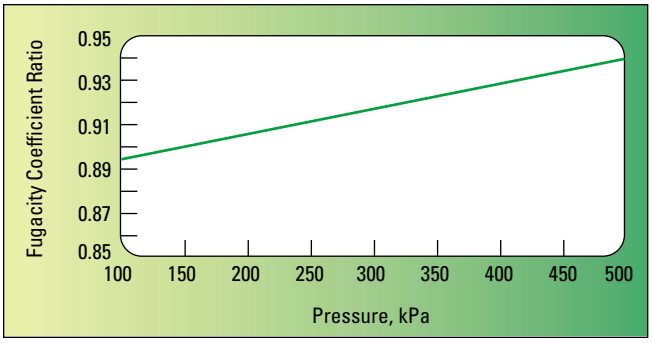

Figure 3. Ratio of the fugacity coefficients for ethanol at 150°C.

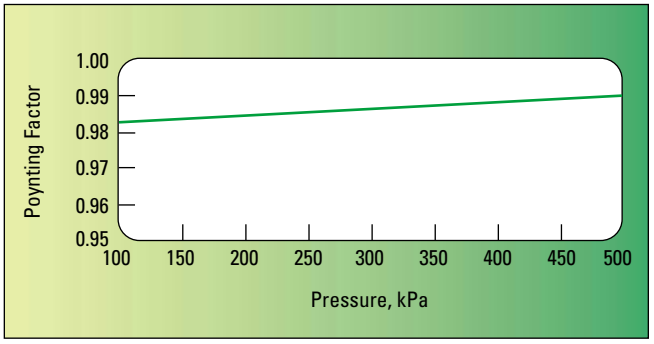

Figure 4. Poynting factor for ethanol at 150°C.

$$y_i = \left(\frac{P_{sat,\,i}}{P}\right)\gamma_i x_i \tag{16}$$

And there we have it, the relationship between the primary factors governing the VLE. This was quite a detour to get to what is the obvious. In our journey, we learned that, as a first approximation, the VLE is dominated by one pure-component property, the vapor pressure, and by a mixture property, the activity coefficient. Stretching it a bit, we can say that the primary variable governing VLE is the vapor pressure:

$$y_i = \left(\frac{P_{sat,\,i}}{P}\right) x_i \tag{17}$$

From this equation onwards, one adds more detail to the model going back to Eq. 11, as shown in Table 2.

Thus, we can think of the problem of creating a reliable thermodynamic model for VLE as providing the correct building blocks for the total equilibrium relationship, Eq. 13. Note that Eq. 5 is the exact equivalent to Eq. 13, but Eq. 5 has the relationships concealed inside the fugacity coefficient expressions. We shall revisit Eq. 5 a bit later. First, let us explore Eq. 13 further.

Equation 13 works up to the critical point of one of the constituents of the mixture, but, beyond that, the equation is undetermined. For example, we do not have a vapor and liquid phase for a pure component beyond the critical point, thus, the vapor pressure contribution is not determined. The same applies to the partial molar volume of the "liquid" phase beyond the critical point. So, how do we proceed?

The easy way out would be to imagine that one could extrapolate the vapor pressure of the component, which is supercritical at the system conditions. Call this component a "solute" to retain the ordinary terminology. Depending upon the solute and the conditions of interest, this extrapolation may be mild (for example, CO_2 and water at ambient conditions) or extreme (H_2 and water at ambient conditions).

Imagine that Eq. 17 applies and, somehow, we can calculate a hypothetical vapor pressure for supercritical components, perhaps by using a simple Antoine equation with its constants *A* and *B* determined at the critical point of the solute so as to match the critical pressure and the slope of the vapor pressure curve (always be very careful when extrapolating expressions such as Eq. 18 beyond the recommended range, because the extended Antoine equation may have a maximum in temperature, and we may have the unpleasant surprise that you can condense nitrogen at ambient pressure by increasing the temperature).

$$\ln P_{sat} = a + \frac{b}{T} \tag{18}$$

$$a = \left(A + \frac{B}{T} + C\ln T + DT^E - \frac{b}{T}\right)_{@Tc} \tag{19}$$

$$b = \left(B - CT - DET^{E+1}\right)_{@Tc} \tag{20}$$

$$\ln P_{sat} = A + \frac{B}{T} + C\ln T + DT^E \tag{21}$$

Using a simple formulation, such as Eq. 14, as the basis for estimating the solubility of gases in liquids, tells us some basic things. First, this simplistic model tells us that the solubility of a gas decreases with temperature. This is usually correct, but not always, as for helium and hydrogen, for example. Second, this model alerts us that the solubility of the solute is independent of the nature of the solvent. This is not correct, but this simple model gets us to the ballpark values when predicting the solubility of solvents and chemically similar solutes as shown by Prausnitz *et al. (8)*, in Table 3.

This approach is qualitative at best, so, how do we proceed? Let us start from the basic definition of the fugacity given by Eq. 10, but with the activity coefficient normalized using the unsymmetric convention:

$$\phi_i^v y_i P = \gamma_i^* x_i f_{i,\,pure}^{\,l} \exp\left(\int_{P_{ref}}^{P} \frac{\bar{v}_i}{RT}\,dP\right) \tag{22}$$

What is meant by unsymmetric normalization? The problem with noncondensables such as nitrogen is that, for the conditions for low-pressure solubility calculations, we cannot condense nitrogen (for all practical purposes, it is a very superheated gas), and the concentration of gas in liquid is very small. Also, the state for the liquid pure-component fugacity for our gas is hypothetical (as for the extrapolated vapor pressure we calculated above). Thus, define the activity coefficient in so it makes more sense for gases by using the following boundary condition:

$$\lim_{x_i \to 0} \gamma_i^* = 1 \tag{23}$$

Table 2. Major relationships for VLE.

Equilibrium is …	Vapor Pressure Contribution	Liquid-Phase Nonideality	Liquid-Phase Compressibility	Vapor-Phase Nonideality
y_i is given by Equation 11	$\left(\frac{P_{sat,\,i}}{P}\right)$	$\gamma_i \exp\int_0^P \frac{\bar{v}_i}{RT}dP$	$\gamma_i \exp\int_0^{P\,sat,j}$	$\frac{\phi_i^s}{\phi_i^v}$
Major variables	Temperature	Temperature and composition (pressure)	Temperature, pressure	Temperature, pressure, and composition

And, we relate the standard state fugacity of the gas with the Henry's law constant:

$$f_{i,pure}^{l} = H_{i,solv}^{Pref} = H_{i,solv}^{Psat,solv} \times \exp\left(\int_{P_{sat,solv}}^{P} \frac{\bar{v}_i^{\infty}}{RT} dP\right) \quad (24)$$

This standard state is special. For subcritical components, the standard state is defined in terms of the component in question alone. For supercritical components, the standard state is defined in terms of the solvent, which dissolves the supercritical component of interest.

$P_{sat,solv}$ is the saturation pressure of the solvent at the system temperature. So, why did we not write it as a saturation pressure? Because the solvent may be a mixture of subcritical substances, and, therefore, we are actually talking about the saturation pressure of a multicomponent mixture of condensables, which, in turn, may require us to calculate activity coefficients. We can combine the standard state definition, pressure dependency, and activity coefficient to yield an expression for the fugacity of a supercritical component:

$$f_i^{l} = \gamma_i^* x_i H_{i,solvent}^{Psat,solv} \exp\left(\int_{solv,\,sat}^{P} \frac{\bar{v}_i^{\infty}}{RT} dP\right) \times \exp\left(\int_{P_{ref}}^{P} \frac{\bar{v}_i}{RT} dP\right) \quad (25)$$

We are not out of the woods yet. Conveniently, we ignored how to calculate $H_{i,solvent}^{Psat,solv}$. Not only is the standard state a function of the solvent, but also is the specific mixture of solvents. Since we do not have a purely theoretical way of calculating the $H_{i,solvent}^{Psat,solv}$, a model is needed. One of the simplest is that of O'Connell *(9)*, which models the interactions between solvents via a one-parameter Margules equation:

$$\ln H_{i,solvent}^{Psat,solvent} = \sum_{\substack{j=1 \\ j\neq i}}^{nc} x_j \ln H_{i,j}^{Pv,j} - \sum_{\substack{j=1 \\ j\neq i}}^{nc} \sum_{\substack{k>j \\ j\neq i}}^{nc} a_{jk} x_j x_k \quad (26)$$

Frequently, process simulators do not use the nonideal correction term, and a_{jk} is assumed to be zero. Also, often,

Table 3. Ideal and actual solubility of several gases in solvents at 25°C (*8*).

	Solubilities in mole fraction x 10^4		
Solute	**Ideal**	***n*-C_7F_{16}**	**CCl_4**
H_2	8	14.01	3.19
N_2	10	38.7	6.29
CH_4	35	82.6	28.4
CO_2	160	208.8	107

$\exp\left(\int_{P_{ref}}^{P} \frac{\bar{v}_i}{RT} dP\right)$ is set to 1. Note that, if we want to use any of the available activity coefficient models created for condensable mixtures, we can relate the symmetric and unsymmetrical activity coefficients using the following relationship:

$$\gamma_i^* = \frac{\gamma_i}{\gamma_i^{\infty}} \quad (27)$$

γ_i^* is the infinite dilution activity coefficient of component *i* calculated using the symmetric convention. A good summary on the use of Henry's law for process calculations is in a series of articles by Carroll *(10–13)*, and more advanced information on Henry's law calculations close to the solvent critical point can be found in the articles by Japas and Levelt Sengers *(14)* and Harvey and Levelt Sengers *(15)*.

We now summarize the basic equations for modeling VLE using activity coefficients for sub- and supercritical components in Table 4. It compares similar functionality for different parts of the total fugacity function in the liquid phase for sub- and supercritical components. The equations in Table 4 provide the basic guidelines for analyzing most VLE problems using activity coefficients. Look at the documentation of your process simulator and you are bound to find Table 4 in one way or another as the basis for activity-coefficient-based models.

Now we get to the interesting part — how to set up the equations so we have data to perform calculations? Some educated simplifications have to be done. Let us look at them step-by-step and see what is necessary.

Vapor-pressure contribution

- Mathematical expression for vapor pressure as a function of temperature — usually some type of Antoine's equation.
- Experimental value of vapor pressure as a function of temperature.
- Estimation method for vapor pressure for components without experimental values.
- Mathematical expression for Henry's constant as a function of temperature — usually some type of Antoine equation.
- Experimental value of Henry's constant for each of the supercritical components in each solvent as a function of temperature.
- Way to estimate the Henry's constant for solute/solvent pairs without experimental data.

Liquid-phase nonideality

- Mathematical model for activity coefficients — Margules, van Laar, Wilson, NRTL, UNIQUAC, etc. …
- Interaction parameters for subcritical/subcritical binary

Table 4. Complete models for phase equilibria using activity coefficients.

Equilibrium is …	Vapor Pressure Contribution	Liquid-Phase Nonideality	Liquid-Phase Compressibility	Vapor-Phase Nonideality
Equation 11	$\left(\frac{P_{sat,i}}{P}\right)$	$\gamma_i \exp\int_{P_{ref}}^{P} \frac{\bar{v}_i^l}{RT}$	$\exp\int_{P_{sat,j}}^{P} \frac{v_i}{RT} dP$	$\frac{\phi_i^s}{\phi_i^v}$
Equation 26	$\frac{H_{i,solv}^{P_{sat,solv}}}{P}$	$\gamma_i^* \exp\int_{P_{ref}}^{P} \frac{\bar{v}_i^l}{RT}$	$\exp\int_{P_{solv,sat}}^{P} \frac{\bar{v}_i}{RT} dP$	$\left(\frac{1}{\phi_i^v}\right)$
Major variables	Temperature	Temperature and composition (pressure)	Temperature, pressure	Temperature, pressure, and composition

pairs determined from experimental data. Except for simple solutions, the interactions are always based on experimental data (do not be fooled by UNIFAC — its parameters were determined using experimental data; there is no real fundamental theory behind them, but, rather, some clever data-fitting).

Liquid-phase compressibility

• Mathematical model for excess liquid molar volumes as a function of composition, temperature, and pressure for subcritical components. Usually, this is not known and the partial molar volumes are assumed to be independent of pressure. Moreover, the partial volumes are supposed to be independent of composition (a thermodynamic oxymoron) and equal to the pure-component molar volumes of the pure components.

• Mathematical model for the infinite-dilution partial molar volume of solute in solvent as a function of temperature and pressure. Except for high-pressure models, this is usually ignored and the infinite-dilution partial molar volume is set to zero. When it has to be used (*e.g.*, when approaching the solvent critical temperature and the infinite-dilution partial molar volume of the solvent cannot be neglected), its value is determined using experimental solubility data.

Vapor-phase nonideality

• Mathematical model for the fugacity coefficient (van der Waals, Redlich-Kwong, Soave-Redlich-Kwong, Peng-Robinson, Virial, …).

• Physical properties necessary for the EOS (usually, but not always — critical temperature, critical pressure, acentric factor, dipole moment, and gas-phase association parameters).

Now, you may be asking yourself: Why have we gone through all the detail about calculations that are done routinely by the simulator on your desktop? If you simply install the software and start running calculations, it is easy to gloss over all of the assumptions that were made in the program. For example, say you are modeling an ethanol facility. You will need data on ethanol, propanol, butanol, pentanols (to model the fuel oils), carbon dioxide (byproduct of sugar fermentation), nitrogen, oxygen, and water. A conventional thermodynamic package to choose would be the NRTL with the virial EOS for the gas phase. So let us proceed, step-by-step, to see how the simulator is going to get ready to perform the first flash (see Table 5).

The simulator is making a series of decisions for you, which may or may not be adequate for the system you intend to model. Naturally, some simulators have sophisticated sets of options for the modification of defaults. These options require more information being required for the model (which you may or may not have — but, at least have the advantage of getting you thinking about what may be important), as well as a whole new set of assumptions that you may or may not be aware of. It should be becoming clear that Table 5 may be more complicated than what we just suggested.

Is simplification possible?

Is there anything thermodynamics can do to help us to have a simpler, less assumption-dependent model? Unfortunately, Eq. 5 is as fundamental as possible without having to propose one or more models and, thus, enter into the realm of molecular thermodynamics. In that, we propose models that are based on more fundamental theories (usually founded upon statistical thermodynamics), but are simplified enough to allow their use in ordinary process calculations — as long as they retain their "physical" flavor.

Perhaps, at the risk of being too simplistic, the techniques used to solve most problems being routinely determined today can be traced back to the work van der Waals started in the 1870s (cubic EOS such as Redlich-Kwong, Soave-Redlich-Kwong, and Peng-Robinson *(16)*, to mention the most popular forms) and the work started in the 1930s and 1940s by Hildebrand and Guggenheim (models based on liquid lattices that were cleverly extended by using the local composition assumption of Wilson *(17)* and further refined by Prausnitz, Renon, and Abrams *(18, 19)* and others).

Certainly, more advanced EOS exist other than the

ones based on the van der Waals model. Still, the additional data needed to use a more advanced model often gains little in accuracy, and we end up using simpler models than expected. Considering the pain of accounting for supercritical components together with subcritical ones, it would be convenient to find a way of working with Eq. 5 directly instead of with standard states and activity coefficients.

Also, we have to determine thermal properties (enthalpy, entropy, and heat capacity) that we routinely need to perform complete material and energy balances. Start by looking at the exact definition of the fugacity coefficient from classical thermodynamics and see if there is another way of solving the problem:

$$RT \ln \phi = \int_V \left[\left(\frac{\partial P}{\partial n_i} \right)_{T, n_{j \neq i}} - \frac{RT}{V} \right] dV - RT \ln Z \qquad (28)$$

Equation 28 is rigorous thermodynamically, and as long as we have a functional relationship between pressure, temperature, volume, and composition, we can calculate fugacity coefficients, and the phase equilibrium problem is (formally) resolved. Before we dig deeper into the these relationships (usually called EOS), it is a good idea to look at some basic thermodynamic relationships that define enthalpy, entropy, and heat capacity:

$$H = H^0 + \int_\infty^V \left[T \left(\frac{\partial P}{\partial T} \right)_{V,ni} + V \left(\frac{\partial P}{\partial V} \right) \right]_{T, ni} dV \qquad (29)$$

$$S = S^0 + \int_\infty^V \left[\left(\frac{\partial P}{\partial T} \right)_{V,ni} - \frac{R}{V} \right] dV + R \ln Z \qquad (30)$$

Table 5. Typical steps for a simple flash calculation.

Action	Reason	Hidden Actions
Choose thermodynamic model, NRTL/Virial	Tell the simulator the basic thermodynamic framework to use to perform equilibrium calculations.	• Select enthalpy, entropy, and heat capacity models. • Partial molar volume for the liquid-phase model is defined. Usually pure-component molar volume is used. • An extrapolation method for the pure-component molar volume beyond T_c is defined. • Mixing rule for $H^{P\ sat,solv}_{i,\ solvent}$ is defined. Usually a_{jk} is set to zero. • Models for liquid and vapor densities are chosen. • Model for transport properties are chosen. • Extrapolation methods for all physical properties are defaulted.
Choose components from component list	Define mixtures that will be potentially present in the simulation.	• Retrieve physical properties from a pure-component database. • Retrieved properties may have been already estimated. Many times estimation criteria are not available. • Missing properties are estimated. Applicability dependent on types of chemicals in the mixture. • Missing $H^{P\ sat,solv}_{i,j}$ are estimated. • Retrieve binary interaction parameters and Henry's constants from a database. Parameters may or may not be applicable to conditions of interest. • Interaction parameters for subcritical binary pairs are estimated (ranging from a simple setting to zero to group contribution methods).
Define pressure, temperature, and bulk composition	Find thermodynamic state of mixture.	• Vapor pressures are calculated. Extrapolations are made if temperature is beyond temperature limits. • Henry's constants are calculated. Extrapolations are done if temperature is beyond temperature limits. • Activity coefficients are calculated. Extrapolations are done usually without any check based on actual data used for determination of interaction parameters. • Enthalpies, entropies, heat capacities are calculated. Depending on the temperature, subcritical components may be crossing their critical temperatures and extrapolations for enthalpy of vaporization are done. • Transport properties are calculated. Usually, very little, if any, experimental mixture information is available to help estimation.

$$C_p = C_p^0 + T\int_{\infty}^{V}\left(\frac{\partial^2 P}{\partial T^2}\right)_V dV - \frac{T\left(\frac{\partial P}{\partial T}\right)_V^2}{\left(\frac{\partial P}{\partial V}\right)_T} - R \qquad (31)$$

Now, we are getting somewhere. If we have an EOS and the ideal-gas heat capacities, we can calculate not only phase equilibria, but also all the needed thermodynamic properties for a comprehensive model of an entire flowsheet. This has a few additional benefits that may not be apparent. For example, we do not have to look for standard states; sub- and supercritical components can be handled using the same framework, and the model approaches the critical point smoothly, thus guaranteeing continuity between liquid and gas states.

Why do we not solve all problems using Eqs. 29–31? We will answer this question in Part II, as well as delve more deeply into EOS and provide tips for simulations. CEP

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Literature Cited

1. "Sulfuric++ User's Manual, Version 2.0," Virtual Materials Group, Inc., Calgary, AB, Canada (2001).
2. **Stanley, P.,** "A Technology Update: Simulation Technology," *Chem. Processing* (Nov. 1997).
3. **Moura, C. A. D., and H. P. Carneiro,** "Common Difficulties in the Use of Process Simulators," *B. Tech. Petrobras,* **34** (3/4) (Jul./Dez. 1991).
4. **Cavett, R. H.,** "Physical Data for Distillation Calculations: Vapor-Liquid Equilibria," *API Proc., Sec. III,* **42** (1962).
5. Design Institute for Physical Property Data (1989).
6. **Lee, B. Y., and M. G. Kesler,** "A Generalized Thermodynamic Correlation Based on Three Parameter Corresponding States," *AIChE J.,* **21** (3) (1975).
7. **Yang, N. S., *et al.,*** "Determine the Number of Theoretical Plates with Commercial Simulators," *Hydrocarb. Proc.* (Aug. 1999).
8. **Prausnitz, J. M., *et al.,*** "Molecular Thermodynamics of Fluid Phase Equilibria," 3rd ed., Prentice-Hall, Englewood Cliffs, NJ (1999).
9. **O'Connell, J. P., and J. M. Prausnitz,** "Thermodynamics of Gas Solubility in Mixed Solvents," *Ind. Eng. Chem. Fund.,* **3** (1964).
10. **Carroll, J. J.** "What's Henry's Law," *Chem. Eng. Progress* (Sept. 1991).
11. **Carroll, J. J.,** "Use Henry's Law for Multicomponent Mixtures," *Chem. Eng. Progress* (Aug. 1992).
12. **Carroll, J. J.,** "Henry's Law — A Historical View," *J. of Chem. Education,* **70** (2) (Feb. 1993).
13. **Carroll, J. J.,** "Henry's Law Revisited," *Chem. Eng. Progress* (Jan. 1999).
14. **Japas, M. L., and J. M. H. Levelt Sengers,** "Gas Solubility and Henry's Law Near the Solvent's Critical Point," *AIChE J.,* **35** (4) (1989).
15. **Harvey, A. H., and J. M. H. Levelt Sengers,** "Correlation of Aqueous Henry's Constants from 0°C to the Critical Point," *AIChE J.,* **36** (4) (1990).
16. **Peng, D. Y., and D. B. Robinson,** "A New Two-Constant Equation of State," *Ind. Eng. Chem. Fund.,* **15** (1976).
17. **Wilson, G. M.,** "Vapor-Liquid Equilibrium. XI: A New Expression for the Excess Free Energy of Mixing," *J. Am. Chem. Soc.,* **86** (1964).
18. **Renon, H., and J. M. Prausnitz,** "Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures," *AIChE J.,* **14** (1968).
19. **Abrams, D. S., and J. M. Prausnitz,** "Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible System," *AIChE J.,* **21** (1975).

R. AGARWAL is executive vice-president of Virtual Materials Group Inc., Calgary, AB, Canada (Phone:(604) 253-9473; Fax: (413) 556-2730; E-mail: Rajeev@VirtualMaterials.com). He has extensive experience creating computer models from first-principle mathematical equations. He is an expert in process optimization, developing unit operation models, and modeling large flowsheets, operating both in steady-state and dynamic modes. At Hyprotech Ltd., he was instrumental in the design and implementation of the dynamic models in Hyprotech's Process Engineering System HYSYS. There, he did high-level system design and implemented object-oriented dynamic models for unit operations with emphasis on operator training. He is a licensed professional engineer and holds an MASc from the University of Toronto in chemical engineering.

Y.-K. LI is vice-president, development of Virtual Materials Group, Inc., Calgary, AB, Canada (Phone: (403) 288-3587; Fax: (520) 222-4943; E-mail: YauKun@VirtualMaterials.com). He holds an MEng from McGill University in chemical engineering and is a registered professional engineer in Alberta, Canada. Li has extensive experience in computational thermodynamics and large-scale process and reservoir simulation.

O. SANTOLLANI is president of Virtual Materials Group, Inc., Calgary, AB, Canada (Phone:(403) 241-8018; eFax/eVoice: (800) 854-3804; E-mail: oscar@virtualmaterials.com; Website: www.virtualmaterials.com), a software solution provider for modeling of physical properties. He has 15 years of experience in various sales, engineering, and marketing positions for Soteica S.R.L., Hyprotech Europe S.L., and Hyprotech Ltd. He holds a degree in chemical engineering from the University of Buenos Aires and is an associate member of AIChE.

M. A. SATYRO is chief technology officer of Virtual Materials Group, Inc. Calgary, AB, Canada (Phone: (403) 241-3929; Fax: (403) 241-3929; E-mail: marco@virtualmaterials.com). He has 16 years of experience in applied thermodynamics, distillation design, and scientific software development. He is also the president of SEA++ Inc., where he has developed software for petroleum refineries and other CPI segments, consulted extensively on thermodynamics applied to the solution of industrial problems, and written several physical property packages. Before that, he was manager of Hyprotech's Applied Thermodynamics and HYCON groups, where he created and supported major commercial process simulation products. He holds a degree in chemical engineering from the University of Sao Paulo and a PhD from the University of Calgary. He is a member of AIChE, and ACS, and is a licensed professional engineer in Alberta.

A. VIELER heads Simulation Engineering, Krimpen, The Netherlands (Phone:(31180550555; Fax: 31180550220; E-mail: andrewvieler@compuserve.com). He has been working in steady-state and dynamic process simulation for 20 years. He has supported, trained users, developed plant models, and consulted with most of the major simulation programs in many areas of the process and pipeline industries, including oil and gas production, oil refining, petrochemicals, and chemical and aqueous process modelling. He has taught many process modeling and simulation courses in the Eastern Hemisphere. He is a member of AIChE.